

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Method of Increasing the Molecular Weight of Polyesters, Polyesteramides or Polyamides

We, WINGFOOT CORPORATION, a corporation organized under the laws of the State of Delaware, United States of America, with offices at 1144, East Market Street, Akron, Ohio, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the preparation of polymers and more particularly to the preparation of polymers of high molecular weight by coupling or interlinking polymers of lower molecular weight by means of a particular type of interlinking agent.

In many instances, while it is relatively easy to prepare polymers of moderate molecular weight, it is much more difficult to prepare polymers of high molecular weight. Thus, in preparing superpolyamides or superpolyesters, and particularly in the latter case, it is often difficult to carry the reaction to completion. Thus, polymers of sufficiently high molecular weight to have the desired properties, for example for the production of fibers, plastics or films, cannot easily be prepared.

The preparation of polymeric ethylene terephthalate of high molecular weight has been a particularly difficult problem. It is impossible to prepare superpolymeric ethylene terephthalate by direct esterification of terephthalic acid with the equivalent amount of ethylene glycol. This is due in part to the insolubility of the terephthalic acid in the reaction mixture. Furthermore, as is well known in the art, such esterifications are catalyzed by acids. Therefore, as the esterification approaches completion, with a corresponding decrease in the

number of carboxyl groups present, the rate of esterification becomes very slow. Thus, ethylene terephthalate polymers prepared from the acid and glycol are usually of low or at most intermediate molecular weight. Ethylene terephthalate superpolymers have been prepared previously by time-consuming ester interchange reactions. In such methods, the preparation of the low polymers may be carried out by direct reaction of the acid with excess amounts of the glycol. The excess of glycol employed functions as a solvent for the highly insoluble acid and the reaction may be catalyzed by such acids or acid forming materials as zinc chloride, *p*-toluene sulfonic acid, or sulfamic acid. After complete solution of the acid has been obtained, the reaction mixture, containing the low molecular weight polymers, is heated above the boiling point of the glycol, frequently under high vacuum, until superpolyesters are formed. Alternatively, alkyl or aryl esters of terephthalic acid may be reacted with ethylene glycol in the presence of ester interchange catalysts, including sodium methylate, magnesium, lithium and metals of the alkaline earth type. Although this method has proven successful for the preparation of the polymers, the time involved is quite long and serious difficulties may be encountered in particular cases with side reactions producing undesirable products.

According to the invention a polyester or polyamide or polyester-amide having at least two radicals selected from amino radicals with at least one reactive hydrogen and hydroxyl radicals is treated with an interlinking agent which is a polylactam, in which two or more lactams are linked by their N atoms with the acyl radical of a polycarboxylic acid. The latter class of compounds is described in 90

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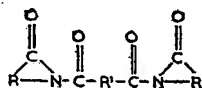
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U.S. Patent 2,303,177 to Schlack which states that they react with hydroxy and amino containing compounds and also suggests the reaction of these compounds with other monomeric compounds to form polymers which may be 2- or 3-dimensional depending on the number of functional groups in the monomers. The amino radicals in the polymers must contain at least one reactive hydrogen and are preferably primary amino. If the intermediate polymer which is the starting material of this invention contains only two reactive groups and the interlinking agent is bifunctional, the resulting high polymer will be linear, and hence thermoplastic. Cross-linked polymers are prepared by the use of a polymer and interlinking agent, one or both of which have more than two reactive groups.

The N-acyl poly lactams, when derived from dicarboxylic acids may be called N-acyl bis lactams and may be represented by the structural formula.



in which



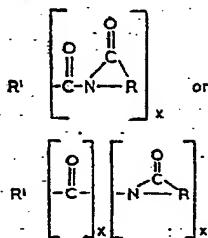
in a lactam radical and



30

in a diacyl radical. More broadly, when the polycarboxylic acid has x carboxyl groups, the products may be represented by the structural formula.

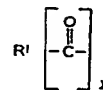
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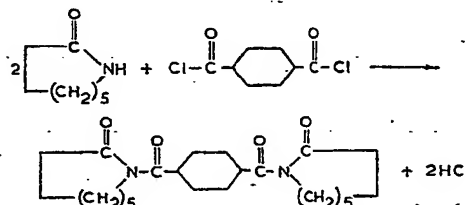


is a lactam radical and



is a polyacyl radical and x is 2 or more, R and R' being organic radicals.

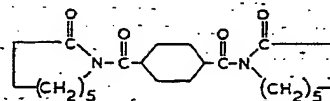
The poly lactam interlinking agents may be prepared by condensing a lactam with the polyacyl chloride or polyacyl bromide of a polycarboxylic acid, the lactam being used in such proportions as to replace each of the halogens in the acyl halide. The reaction may be illustrated by the following equation, employing epsilon caprolactam and terephthalyl chloride as representative reactants:



The preparation of such compounds is illustrated by the following representative example.

EXAMPLE 1.

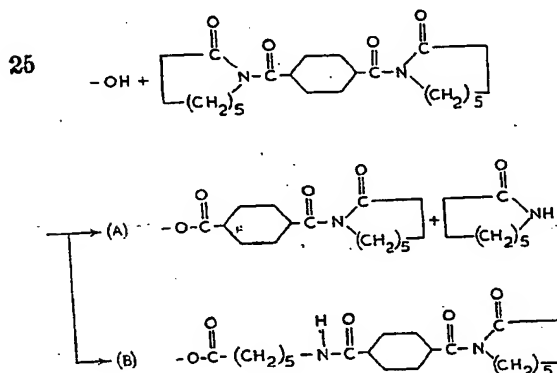
To a solution of 22.6 grams (0.20 mol.) of epsilon caprolactam in 200 cubic centimeters of dioxane were added a solution of 20.8 grams (0.102 mol.) of terephthalyl chloride in 100 cubic centimeters of dioxane and 20.2 grams (0.20 mol.) of triethylamine in 50 cubic centimeters of dioxane. After these additions has been completed, the mixture was heated at 100° C. for 4 hours. It was then cooled and the triethylammonium chloride was filtered off. Concentration of the filtrate yielded a brown oil which on treatment with a mixture of ethyl acetate and hexane yielded a solid precipitate. After extraction with ethyl acetate, the precipitate was recrystallized from alcohol. The product, N,N'-terephthalyl bis-caprolactam, having the formula



melted at 191–193° C. the calculated analysis for this compound is carbon-67.42%, hydrogen-6.74%. The values found by actual analysis were carbon-67.01%, hydrogen-6.84%.

Further examples of N-acyl poly lactams are N,N'-isophthalyl bis epsilon caprolactam, N,N'-adipyl bis epsilon caprolactam, N,N'-adipyl bis valero-
 5 lactam, N,N'-isophthalyl bis valero-
 lactam, N,N'-isophthalyl bis butyro-
 lactam, N,N'-terephthalyl bis butyro-
 lactam, N,N'-2,5-dichloroterephthalyl
 bis caprolactam, N,N',N''-trimesyl tris
 10 epsilon caprolactam, the tetra valero-
 lactam of 1,4,5,8-naphthalene tetracarboxylic acid, the tetra epsilon caprolactam of cyclohexanonetetrapropionic acid, the tetra epsilon caprolactam of dicyclohexanoneoctapropionic acid and the poly-
 15 caprolactam of polyacrylic acid.

The interlinking process may proceed according to either or both of the following illustrative equations, in which —OH
 20 represents one end of a low molecular weight polymer having terminal hydroxyl groups and N,N'-terephthalyl bis caprolactam is shown as a typical N-acyl polyactam of a polycarboxylic acid.



The mechanism of the reaction is not known for certain and it is possible that both of the indicated types of reaction
 30 occur. It appears that the reaction takes place at least in part according to equation (A) since some free lactam is formed and can be recovered and identified. In the equations, reaction has been shown on
 35 only one end of each of the starting materials. Similar reaction can and, in practice, does take place on both ends of the molecules.

Although the invention is applicable to
 40 polymers containing two or more hydroxyl and/or amino terminal groups, the invention is particularly useful in the preparation of polyesters. The various superpolyesters derived from tere-
 45 phthalic or isophthalic acid and polymethylene glycols containing from two to ten methylene groups, including the ethylene, trimethylene, tetramethylene, pentamethylene, hexamethylene and deca-

methylene glycols and similar copoly-
 50 esters, may be treated by this method. Also, polyesters derived from the above acids and branched chain glycols as well as glycols containing either oxygen or
 55 sulfur atoms as integral parts of the chain separating the two hydroxyl groups can be treated by this method. Other useful
 polyesters are those derived from the various polymethylene glycols containing
 60 from two to ten carbon atoms and acids such as diphenoxyethane-4,4'-dicarboxylic acid, diphenoxypropane-4,4'-dicarboxylic acid, diphenoxybutane-4,4'-dicarboxylic acid, diphenoxypentane-4,4'-dicarboxylic acid, diphenoxyhexane-4,4'-dicarboxylic acid, diphenylmethane-4,4'-dicarboxylic acid, diphenylbutane-4,4'-dicarboxylic acid, naphthalene-1,5-dicarboxylic acid, naphthalene-2,6-dicarboxylic acid, naphthalene-2,7-dicarboxylic
 70 acid, 1,4-diphenoxybenzene-4',4''-dicarboxylic acid, 1,4-bis-(phenoxyethyl) benzene-4',4''-dicarboxylic acid, phenoxybenzene-4,4'-dicarboxylic acid, diphenylthioether-4,4'-dicarboxylic acid
 75 and diphenyl-4,4'-dicarboxylic acid.

As is well known in the art, linear aliphatic superpolyamides derived from diamines and dibasic acid in which the
 80 number of chain atoms in the polymeric repeat unit is greater than eight are usually fusible and thermoplastic and are useful in the form of fibers, bristles, monofilaments, films and plastics. These
 85 polymers are readily treated by the methods of this invention. In addition, polyamides derived from aromatic dibasic acids and diamines or by the self-condensation of amino acids may readily
 90 be interlinked with N-acyl polyactams to produce superpolyamides.

A particularly important and valuable application of the invention is in the production of linear polymers of high molecular weight. For example, it is frequently difficult to obtain linear poly-
 95 esters (of the glycol-dicarboxylic acid type) having molecular weights sufficiently high for optimum physical properties. Direct esterification of dicarboxylic acid and glycol proceeds slowly,
 100 particularly when the molecular weight becomes moderately large. Reaction of the glycol with a dicarboxylic acid chloride is much faster but is inapplicable
 105 to certain types and in other cases it may be preferred to avoid use of the acid chloride because of unavailability or because of the deleterious effects of the hydrogen chloride released during the reaction. According to the present invention,
 110 a polyester or polyamide or polyesteramide of low or moderate molecular weight having hydroxyl and/or amino

end groups can be converted within a relatively short period of time to a polymer of high molecular weight.

Various methods are available for preparing low polymers with terminal hydroxyl and/or amino end groups. For example, a dicarboxylic acid can be reacted with more than an equivalent proportion of glycol and/or diamine. Small excesses produce larger polymer molecules while large excesses produce smaller molecules. Some polyesters can also be prepared by reacting an excess of glycol with an acid chloride. Polyamides can also be prepared by self-polymerization of a mono-aminomonocarboxylic acid in the presence of a diamine. Polyesters can be prepared similarly from a monohydroxymonomocarboxylic acid and a glycol. Polyesters can also be prepared by an ester interchange reaction between a glycol and an alkyl or aryl ester of a dicarboxylic acid. The particular method for forming the "intermediate" polymer having terminal amino and/or hydroxyl groups is not part of the present invention, which is directed to the interlinking of such polymers, however formed.

In order to produce polymers of high molecular weight or superpolymers, the number of hydroxyl and/or amino groups and the acylating groups arising from the N-acyl polylactam interlinking agent must be approximately equal. In the preparation of linear polymers, this will involve equimolecular proportions. If the average molecular weight of the starting polymers is known, the approximate amount of interlinking agent can be calculated. In practice, however, it is frequently desirable to establish the optimum amount of interlinking agent by empirical methods. Because of the difference in size of the molecules of "intermediate" polymer and interlinking agent, the proportion by weight of the interlinking agent will be small. If the molecular weight of the polymer to be interlinked is low, larger amounts of the relatively expensive interlinking agent will be required. The interlinking agent may be charged into a reactor containing well-stirred molten polymer and the reaction continued at temperatures above the melting point of the polymer. After the initial reactions have been completed, the liberated lactam may be removed under reduced pressure and the resultant superpolymer removed by any suitable means. Alternatively, the interlinking agent may be added portionwise with complete reaction before the next addition. Under these conditions, the addition of an amount of N-acyl poly-

lactam in excess of the calculated amount will not be harmful providing the molecular weight of the polymer at the end of the previous reaction period was sufficiently high to give the desired properties. An excellent method of carrying out the reaction is to add the N-acyl polylactam or its solution to a solution of the polymer in a nonreactive solvent. Under these conditions, thorough mixing is assured. The reaction can be completed at an elevated temperature. The polymer may be recovered either by distillation of the solvent or by precipitating of the polymer in a nonsolvent.

The practice of the invention in the preparation of linear polymers is illustrated by the following examples.

EXAMPLE 2.

A low viscosity decamethylene sebacate polymer was prepared by reacting sebacyl chloride with an 8.0% molar excess of decamethylene glycol in *o*-dichlorobenzene solution. After two hours at reflux, the solvent was distilled off under reduced pressure. The residual polymer had a melt viscosity of 6.33 poises at 109° C. From this viscosity, the molecular weight was calculated to be 3,200.

A small portion (4.148 grams) of this low molecular weight polymer was reacted with 0.459 gram of N,N'-isophthalyl-bis-caprolactam by refluxing in *o*-dichlorobenzene for one and a half hours. After removal of the solvent, the residual polyester had a melt viscosity of 3,246 poises at 109° C. Fibers drawn from the melt cold drew readily.

EXAMPLE 3.

A low molecular weight polyamide was prepared by heating 4.49 grams of sebacic acid and 4.09 grams (7.0% excess) of decamethylene diamine at 218° C. for two hours, with pure nitrogen passing through the melt. At the end of this time, the viscosity had reached a fairly constant value of 70 poises, corresponding to a molecular weight of about 6,000. Four hundred and forty-three thousandths gram of N,N'-terephthalyl-bis-caprolactam was then added to the polymer. On heating at 255° C., the viscosity rose very rapidly and within a half hour reached a value in the vicinity of 30,000 poises.

EXAMPLE 4.

A low molecular weight ethylene terephthalate polymer was prepared by a magnesium catalyzed ester interchange reaction from 15.0 grams of dimethyl terephthalate and 7.275 grams of ethylene glycol. The reactants were heated at 197° C. for one and a half hours with nitrogen stirring and the excess glycol was then removed by heating in a vapor bath main-

tained at 280° C. for one and a half hours. The very low polymer was then heated at 280° C. *in vacuo* and ethylene glycol gradually distilled away from the molten polymer. The viscosity of the polymer continued to rise under these conditions, the melt viscosity after 1.33 hours at this temperature being 20.7 poises, corresponding to an estimated molecular weight of 4,800. The cooled polymer was crushed into fine pieces and 4.5 grams of this polymer and 0.334 grams of N,N'-isophthalyl-bis-caprolactam were added to 15 milliliters of *o*-dichlorobenzene. This mixture was heated at reflux for two hours and the solvent distilled off. After heating *in vacuo* at 280° C. for one hour, the melt viscosity of the polymer was 2,240 poises. The molten polymer cooled to a light yellow crystalline solid, melting at 252—255° C. Fibers formed from the molten polymer would cold draw and were pliable and strong.

EXAMPLE 5.

To prepare a low molecular weight tetramethylene terephthalate polymer with hydroxyl end groups, 40.56 grams of terephthalyl chloride in 120 milliliters of *o*-dichlorobenzene were reacted with 18.73 grams of tetramethylene glycol. The reactants were heated at 61° C. for two hours with agitation by a stream of dry nitrogen and were then refluxed for an additional four hours. The solvent was removed by distillation, the last traces being removed by heating *in vacuo* at 241° C. for one hour. The polymer had a melt of 60 poises at 241° C. and cooled to a light cream colored crystalline solid. To 4.86 grams of the crushed polymer were added 0.2172 gram of N,N'-isophthalyl-bis-caprolactam and 15 milliliters of *o*-dichlorobenzene and the mixture was heated to reflux under dry nitrogen for six hours. The solvent was then removed by distillation, the last traces of solvent, as well as a few bubbles, being removed by heating *in vacuo* at 241° C. for one hour. The resulting polymer had a melt viscosity of 2,300 poises at 241° C.

EXAMPLE 6.

Low molecular weight hexamethylene terephthalate was prepared by condensing 3.76 grams of hexamethylene glycol with 6.091 grams of terephthalyl chloride in the presence of 18 milliliters of *o*-dichlorobenzene. The condensation was initially carried out at 61° C. for one hour and then at reflux for two and a half hours under dry nitrogen. The polymer was isolated by distillation of the solvent and was heated under vacuum at 218° C. for one hour to remove the last

traces of solvent and to free the molten polymer of entrapped gases. The viscosity of the polymer was 16.15 poises at this temperature and the calculated molecular weight (assuming a glycol loss of 0.4 mol %) was 4,460. To 7.44 grams of the above polymer dissolved in 18 milliliters of *o*-dichlorobenzene was added 0.5931 gram of N,N'-terephthalyl-bis-caprolactam and the mixture was refluxed for two hours under dry nitrogen. Isolation of the polymer was accomplished by distillation, the polymer being freed of traces of solvent by heating *in vacuo* at 218° C. for two hours. The resulting polymer had a melt viscosity of 1,300 poises and, on cooling, was a light brown crystalline solid.

EXAMPLE 7.

In the preparation of hydroxyl terminated decamethylene terephthalate intermediate polymer, 37.64 grams of decamethylene glycol were reacted with 40.61 grams of terephthalyl chloride. The condensation was carried out in the absence of a solvent by heating the reactants at 110° C. for half an hour and then increasing the temperature to 218° C. for one and a half hours under atmospheric pressure and finally heating for one and half hours at 218° C. under vacuum. The polymer had a melt viscosity of 10.83 poises and a calculated molecular weight of 3,950. The reaction between the interlinking agent and the hydroxyl terminated polymer was carried out in the melt in the absence of solvent. To 4.92 grams of the polymer in a reaction tube having a diameter of 22 millimeters was added 0.4414 gram of N,N'-terephthalyl-bis-caprolactam and the entire assembly was carefully flushed with dry nitrogen. The tube was heated in a 218° C. vapor bath and solution of the interlinking agent in the polymer was completed within five minutes. The viscosity of the melt rose rapidly and in two and a half hours the viscosity had reached 12,100 poises at 218° C. On cooling, a light colored crystalline solid resulted. In the upper end of the reaction tube a considerable amount of sublimate was observed. This sublimate melted at 69—71° C., indicating that caprolactam is one of the products of the reaction.

EXAMPLE 8.

In order to prepare a low molecular weight tetramethylene isophthalate suitable for interlinking, 19.805 grams of tetramethylene glycol were reacted with 42.493 grams of isophthalyl chloride in the presence of 120 milliliters of *o*-dichlorobenzene. After carefully adjusting the flow of dry nitrogen to ensure adequate stirring, the reactants were

heated at 61° C. for two hours and then under reflux for four and a half hours. The solvent was removed by distillation and, after heating for one hour at 218° C., the polymer was free of solvent and bubbles. The melt viscosity of this polymer was 15.1 poises at 218° C. and the calculated molecular weight was 7,000.

The interlinking reaction was carried out by reacting 5.005 grams of the above polymer with 0.2239 gram of N,N'-isophthalyl-bis-caprolactam in the presence of 15 milliliters of *o*-dichlorobenzene at reflux temperature for six hours. After removing the solvent by distillation and freeing it of the last traces of solvent and all bubbles by heating for two and a half hours at 218° C., the melt viscosity of the polymer was 3,320 poises. The cooled polymer was a light yellow solid.

Cross-linked polymers having properties similar to those of a vulcanized rubber or a gelled or thermoset resin can be prepared by the process of the invention when either or both the N-acyl polylactam and the "intermediate" polymer contain more than two functional groups. For example, such products result when a linear polyester or polyamide or polyesteramide having hydroxyl and/or amino end groups is treated with an N-acyl polylactam compound having three or more lactam groups per molecule. Another method for preparing cross-linked or network polymers is by reacting a nonlinear polyester, polyamide or polyesteramide containing more than two amino and/or hydroxyl groups per molecule with an N-acyl polylactam containing at least two lactam groups per molecule. Suitable nonlinear polymers may be prepared, for example, by condensing a glycol, dibasic acid and a polycarboxylic acid having a functionality greater than two or by condensing a glycol, a polyhydric alcohol having a functionality greater than two and a dicarboxylic acid. In preparing these initial polymers, it is preferred to use a sufficient amount of glycol to prevent gelation of the composition of the esterification process or, if gelation does occur, the condensation preferably should not proceed to an extent beyond the gelation point such that the product cannot be milled or molded or otherwise processed in the subsequent interlinking reaction. The proportion of the glycol required for a given amount of the polyfunctional compound may be determined by trial or it may be computed approximately from theory. (See JACS, Volume 63, page 3083 (1941)). Further examples of suitable polymers having a functionality greater than two are those of the

"multichain" type prepared by reacting a relatively small amount of an alcohol containing at least three reactive hydroxyl groups with a relatively large amount of a monohydroxy monocarboxylic acid or by reacting a relatively small amount of a polyamino compound containing at least three reactive amino groups with a relatively large amount of a monoaminomonocarboxylic acid or a monohydroxymonocarboxylic acid. Such polymers are described in United States Patent Specifications Nos. 2,524,045 and 2,524,046. The nonlinear, preferably thermoplastic, polymer prepared according to one of these methods, or any other method, is then treated with a polylactam compound having a functionality of at least two. It is preferred to use a proportion of this compound which is approximately equivalent to the hydroxyl or amino groups present in the polymer. This polylactam compound is incorporated by stirring, milling or by dissolving in a suitable solvent. This mixture can be molded or cast into the form of the final object and reaction effected by heating at elevated temperature.

The polylactam compound is preferably used in an amount approximately in stoichiometric equivalence with the reactive hydroxyl and/or amino groups in the polymer.

Thus, the invention includes the conversion of thermoplastic polymers having at least two hydroxyl and/or amino groups per molecule to "vulcanized" or thermoset compositions through treatment with polylactam compounds as described above. If the initial polymer molecules contain only two hydroxyl and/or amino groups per molecule, as in the case of linear polymers terminated with hydroxyl and/or amino groups, a polylactam compound containing at least three lactam groups must be used in order to achieve cross-linking. If the number of available hydroxyl and/or amino groups per molecule is three or greater, either the bis- or higher polylactam compounds may be used.

The practice of the invention in preparing cross-linked polymers is illustrated by the following representative example.

EXAMPLE 9.

A low molecular weight polymer was prepared by reaction of 6.651 grams of decamethylene glycol, 0.353 gram of pentaerythritol and 5.845 grams of adipic acid at 160° C. with nitrogen stirring for sixteen hours. The melt viscosity of the low viscosity polymer was 24.05 poises at 109° C.

Reaction of this polymer (4.21 grams) with N,N'-isophthalyl-bis-caprolactam (0.31 gram) was carried out in *o*-dichlorobenzene. On refluxing, the solution thickened rapidly, and after 45 minutes, insoluble gel was formed. The solvent was distilled off under reduced pressure. The residual polymer did not flow at temperatures below the range of thermal decomposition. The product was insoluble in chloroform, toluene, *o*-dichlorobenzene and diphenyl ether.

What we claim is:—

1. A method for increasing the molecular weight of a polyamide or polyester or polyesteramide containing at least two radicals selected from amino radicals with at least one reactive hydrogen atom and from hydroxyl radicals characterized by reacting said polymer with an N-acyl polylactam in which two or more lactams are linked by their N-atoms with the acyl radical of a polycarboxylic acid.
2. A method as claimed in claim 1 in which the N-acyl polylactam is used in an amount equivalent to said hydroxyl and/or amino radicals.
3. A method as claimed in any of claims 1 or 2 in which the lactam is an N,N'-acyl bis lactam of a dicarboxylic acid.
4. A method as claimed in claim 1, 2 or 3 in which the polymer contains two radicals selected from amino radicals with at least one reactive hydrogen atom and from hydroxyl radicals.
5. A method as claimed in claim 1, 2 or 3 in which the polymer to be reacted is a linear polyester containing terminal hydroxyl radicals.
6. A method as claimed in claim 5 in which the polyester is polymeric ethylene terephthalate.
7. A method as claimed in claim 6 in which the lactam is an N,N'-isophthalyl bis caprolactam.
8. A method as claimed in claim 6 in which the lactam is an N,N'-terephthalyl bis caprolactam.
9. A method as claimed in claim 1 in which the polymer to be reacted is a linear polyamide containing terminal amino radicals.
10. A method for increasing the molecular weight of a polyester or polyamide or polyester-amide containing at least two radicals selected from hydroxyl radicals and amino radicals substantially as described with reference to the examples.

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